Supplementary Information for: Exciton Radiative Lifetimes in Layered Transition Metal Dichalcogenides

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Bandstructures

Figure S1 shows the *GW* bandstructures of monolayer MoS_2, WS_2, $MoSe_2$, and WSe_2.

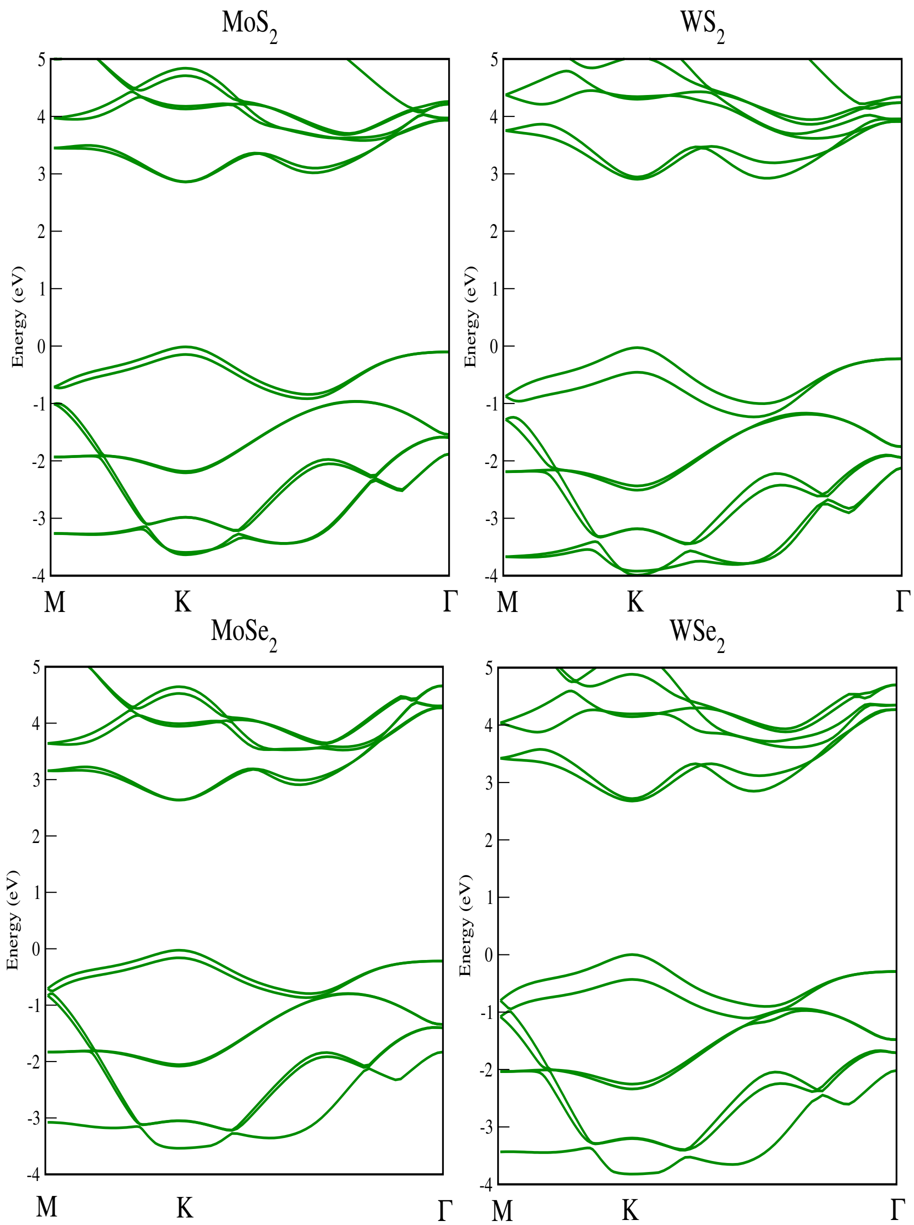

Figure S1. Quasiparticle bandstructures calculated using *GW*.

Derivation of the Exciton Radiative Lifetimes

We assume a system in an initial state $|S(\mathbf{Q}),0\rangle$ with one exciton in state S of momentum $\mathbf{Q}$, and zero photons. We employ Fermi's Golden Rule to compute the radiative decay rate $\gamma_S(\mathbf{Q})$ of the initial state to the electronic ground state $|G,1_{\mathbf{q},\lambda}\rangle$, which has no excitons and one photon of momentum $\mathbf{q}$ and polarization λ:[1]

$$\gamma_S(\mathbf{Q}) = \frac{2\pi}{\hbar} \sum_{\mathbf{q},\lambda} |\langle G, 1_{\mathbf{q},\lambda}|H_{int}|S(\mathbf{Q}),0\rangle|^2 \, \delta(E_S(\mathbf{Q}) - \hbar c q) \tag{1}$$

where $E_S(\mathbf{Q})$ is the energy of the exciton in state S of momentum $\mathbf{Q}$, c is the speed of light, and δ is Dirac's delta function. Using the dipole approximation for the interaction H_{int} between electrons and photons, and following steps similar to Spataru et al.,[1] we obtain:

$$\gamma_S(\mathbf{Q}) = \frac{2\pi}{\hbar}\frac{e^2}{m^2c^2}\frac{2\pi\hbar c}{V}\left(\sum_{\mathbf{q},\lambda}\frac{1}{q}\left|\sum_{v,c,\mathbf{k}} A^{(S)}_{v,c,\mathbf{k}}(\mathbf{Q})\,\langle v,\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}\mathbf{e}_{\mathbf{q},\lambda}\cdot\mathbf{p}|c,\mathbf{k}+\mathbf{Q}\rangle\right|^2\right)\delta(E_S(\mathbf{Q}) - \hbar c q) \tag{2}$$

where m is the electron mass, V the volume of the system, v and c label the valence (occupied) and conduction (empty) bands, respectively, and $\mathbf{k}$ is the crystal momentum in the Brillouin Zone (BZ) labeling the Kohn-Sham states in the bra and ket of eq. 2. In addition, $\mathbf{e}_{\mathbf{q},\lambda}$ are two arbitrarily chosen and mutually orthogonal polarization unit vectors of the photon, both of which are orthogonal to $\mathbf{q}$, and $A^{(S)}_{v,c,\mathbf{k}}(\mathbf{Q})$ are the BSE expansion coefficient of the two-particle exciton state $|\Psi_S(\mathbf{Q})\rangle$ in terms of single-particle Kohn-Sham states, namely, $|\Psi_S(\mathbf{Q})\rangle = \sum_{v,c,\mathbf{k}} A^{(S)}_{v,c,\mathbf{k}}(\mathbf{Q})\,|v,\mathbf{k}\rangle\,|c,\mathbf{k}+\mathbf{Q}\rangle$.

For a two-dimensional material − here in the xy plane − the in-plane components of the photon momentum $\mathbf{q} = (q_x, q_y, q_z)$ and the 2D exciton momentum $\mathbf{Q} = (Q_x, Q_y, 0)$ are equal due to momentum conservation, as seen by applying applying the properties of Bloch states to the dipole matrix elements:

$$\langle v,\mathbf{k}|e^{-i\mathbf{q}\cdot\mathbf{r}}\mathbf{e}_{\mathbf{q},\lambda}\cdot\mathbf{p}|c,\mathbf{k}+\mathbf{Q}\rangle \;\approx\; \mathbf{e}_{\mathbf{q},\lambda}\cdot\langle v,\mathbf{k}|\mathbf{p}|c,\mathbf{k}\rangle\,\delta_{q_x,Q_x}\delta_{q_y,Q_y} \tag{3}$$

where given the small photon momentum compared to the size of the BZ, both $\mathbf{q} \to 0$ and $\mathbf{Q} \to 0$. Due to depolarization along the plane-normal direction,[1] the matrix element of p_z is vanishingly small, so that only light polarized in the xy plane can be absorbed. In addition, when summed over the Brillouin zone, the contributions from the matrix elements of p_x and p_y are identical for the TMDs due to symmetry. We thus get:

$$\sum_{v,c,\mathbf{k}} A^{(S)}_{v,c,\mathbf{k}} \langle v,\mathbf{k}| e^{-i\mathbf{q}\cdot\mathbf{r}} \mathbf{e}_{\mathbf{q},\lambda}\cdot\mathbf{p}|c,\mathbf{k}+\mathbf{Q}\rangle \approx \mathbf{e}_{\mathbf{q},\lambda}\cdot(\hat{\mathbf{x}}+\hat{\mathbf{y}})\delta_{q_x,Q_x}\delta_{q_y,Q_y}\sum_{v,c,\mathbf{k}} A^{(S)}_{v,c,\mathbf{k}} \langle v,\mathbf{k}|p_{\parallel}|c,\mathbf{k}\rangle \quad (4)$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are the x-axis and y-axis unit vectors, respectively, and $p_{\parallel}$ the momentum operator in an arbitrary in-plane direction. We substitute these matrix elements in eq. 2, use δ_{q_x,Q_x} and δ_{q_y,Q_y} to eliminate the sums over q_x and q_y, express the volume in terms of the in-plane area A and the plane-normal length L_z of the system ($V = AL_z$ is the volume), and use the identity $\sum_{q_z} = \frac{L_z}{2\pi}\int_{-\infty}^{\infty} dq_z$ to obtain:

$$\gamma_S(\mathbf{Q}) = \frac{2\pi e^2}{m^2c^2\hbar}\frac{\left|\langle G\,|\,p_{\parallel}\,|\,\Psi_S(0)\rangle\right|^2}{A}\sum_{\lambda}\int_{-\infty}^{\infty} dq_z\,\frac{1}{q}\left|\mathbf{e}_{\mathbf{q},\lambda}\cdot(\hat{\mathbf{x}}+\hat{\mathbf{y}})\right|^2\delta\left(\frac{E_S(\mathbf{Q})}{\hbar c}-q\right) \quad (5)$$

with $\mathbf{q} = (Q_x, Q_y, q_z)$ and $q = \sqrt{q_z^2+Q^2}$ (where $Q^2 = Q_x^2 + Q_y^2$).

The $\mathbf{q}$-dependence of the polarization vector needs to be taken into account carefully to solve the integral in eq. 5.[1] To this end, we introduce the unit vector $\hat{\mathbf{u}}$ in the $x = y$ direction, $\hat{\mathbf{u}} = (\hat{\mathbf{x}}+\hat{\mathbf{y}})/\sqrt{2}$, and rewrite the scalar product in eq. 5 as $\mathbf{e}_{\mathbf{q},\lambda}\cdot(\hat{\mathbf{x}}+\hat{\mathbf{y}}) = \sqrt{2}\,\mathbf{e}_{\mathbf{q},\lambda}\cdot\hat{\mathbf{u}}$. We choose one of the two polarization vectors, $\mathbf{e}_{\mathbf{q},1}$, to be in the same plane as $\mathbf{q}$ and $\hat{\mathbf{u}}$, and define the angle θ between $\mathbf{e}_{\mathbf{q},1}$ and $\hat{\mathbf{u}}$ (see Figure S2). With these choices, $\mathbf{e}_{\mathbf{q},1}\cdot\hat{\mathbf{u}} = \cos\theta$, while $\mathbf{e}_{\mathbf{q},2}\cdot\hat{\mathbf{u}} = 0$, so that $\mathbf{e}_{\mathbf{q},2}$ does not contribute to the radiative rate in eq. 5.

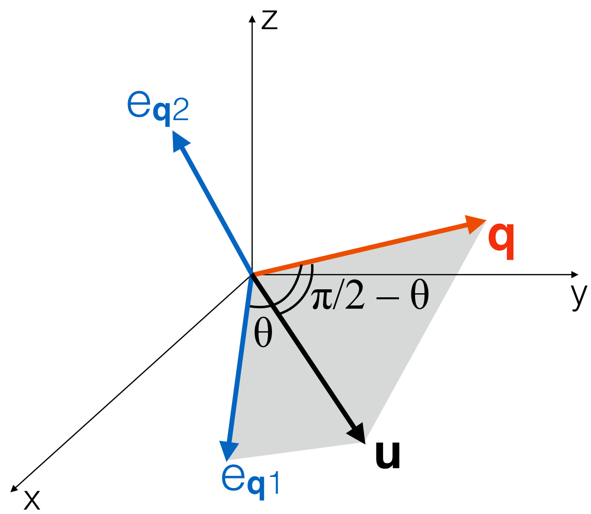

Figure S2. The polarization unit vectors $\mathbf{e}_{\mathbf{q},\lambda}$ are shown in blue, and the photon wavevector $\mathbf{q}$ in red. These three vectors are mutually orthogonal. The unit vector $\hat{\mathbf{u}}$, shown in black, forms an angle θ with $\mathbf{e}_{\mathbf{q},1}$, an angle $\pi/2-\theta$ with $\mathbf{q}$, and is orthogonal to $\mathbf{e}_{\mathbf{q},2}$.

It follows from the definition of $\hat{\mathbf{u}}$ that $\mathbf{q}\cdot\hat{\mathbf{u}} = (q_x+q_y)/\sqrt{2}$, and from Figure S2 that $\mathbf{q}\cdot\hat{\mathbf{u}} = q\sin\theta$. We thus have in eq. 5:

$$|\mathbf{e}_{\mathbf{q},\lambda}\cdot(\hat{\mathbf{x}}+\hat{\mathbf{y}})|^2 = 2\,|\mathbf{e}_{\mathbf{q},1}\cdot\hat{\mathbf{u}}|^2 = 2(1-\sin^2\theta) = \frac{2}{q^2}\left[q^2 - \frac{(q_x+q_y)^2}{2}\right] \tag{6}$$

Substituting in eq. 5, and using $q_x = Q_x$, $q_y = Q_y$, and $q^2 = q_z^2 + Q^2$ (where $Q^2 = Q_x^2 + Q_y^2$), we get:

$$\gamma_S(\mathbf{Q}) = \frac{4\pi e^2}{m^2c^2\hbar}\,\frac{\left|\left\langle G\,\middle|\,p_\parallel\,\middle|\,\Psi_S(0)\right\rangle\right|^2}{A}\int_{-\infty}^{\infty} dq_z\,\frac{q_z^2+\frac{(Q_x-Q_y)^2}{2}}{(q_z^2+Q^2)^{3/2}}\,\delta\!\left(\frac{E_S(\mathbf{Q})}{\hbar c} - \sqrt{q_z^2+Q^2}\right) \tag{7}$$

Similar to Spataru et al.[1] , we define the square of the dipole matrix element μ_S^2 as the velocity (rather than momentum) dipole matrix element computed using the BSE, divided by the number N_k of $\mathbf{k}$-points in the 2D $\mathbf{k}$-point grid used in the calculation:

$$\mu_S^2 = \frac{\hbar^2}{m^2E_S^2(0)}\,\frac{\left|\left\langle G\,\middle|\,p_\parallel\,\middle|\,\Psi_S(0)\right\rangle\right|^2}{N_k} \tag{8}$$

Since the area of the system is $A = A_{uc}N_k$, where A_{uc} is the area of the unit cell used in the calculation:

$$\frac{\left|\left\langle G \,\middle|\, p_\parallel \,\middle|\, \Psi_S(0)\right\rangle\right|^2}{A} = \frac{m^2 E_S^2(0)}{\hbar^2} \frac{\mu_S^2}{A_{uc}} \tag{9}$$

We rewrite eq. 7 as:

$$\gamma_S(\mathbf{Q}) = \frac{4\pi e^2 E_S^2(0)}{c^2\hbar^3} \frac{\mu_S^2}{A_{uc}} I(\mathbf{Q}) \tag{10}$$

where I is the integral:

$$I(\mathbf{Q}) = \int_{-\infty}^{\infty} dq_z \, \frac{q_z^2 + \frac{(Q_x - Q_y)^2}{2}}{(q_z^2 + Q^2)^{3/2}} \, \delta\left(\frac{E_S(\mathbf{Q})}{\hbar c} - \sqrt{q_z^2 + Q^2}\right) \tag{11}$$

Using the properties of the delta function,[2] we can calculate the integral I analytically:

$$I(\mathbf{Q}) = \frac{2}{\frac{E_S^2(\mathbf{Q})}{\hbar^2 c^2}} \left[\frac{\frac{E_S^2(\mathbf{Q})}{\hbar^2 c^2} - \frac{(Q_x + Q_y)^2}{2}}{\sqrt{\frac{E_S^2(\mathbf{Q})}{\hbar^2 c^2} - Q^2}}\right] = \frac{2\hbar^2 c^2}{E_S^2(\mathbf{Q})} \left[\sqrt{\frac{E_S^2(\mathbf{Q})}{\hbar^2 c^2} - Q^2} + \frac{1}{2} \frac{(Q_x - Q_y)^2}{\sqrt{\frac{E_S^2(\mathbf{Q})}{\hbar^2 c^2} - Q^2}}\right] \tag{12}$$

and obtain the radiative rate, eq. 1 in the main text:

$$\boxed{\gamma_S(\mathbf{Q}) = \gamma_S(0) \cdot \left\{\sqrt{1 - \left(\frac{\hbar c Q}{E_S(\mathbf{Q})}\right)^2} + \frac{1}{2} \frac{\left[\frac{\hbar c (Q_x - Q_y)}{E_S(\mathbf{Q})}\right]^2}{\sqrt{1 - \left(\frac{\hbar c Q}{E_S(\mathbf{Q})}\right)^2}}\right\}} \tag{13}$$

where the transition rate for $\mathbf{Q} = 0$ is defined as in eq. 2 in the main text:

$$\boxed{\gamma_S(0) = \frac{8\pi e^2 E_S(0) \mu_S^2}{A_{uc} \hbar^2 c}} \tag{14}$$

To obtain the exciton radiative rate at temperature T, we average the rates up to the maximum momentum Q_0 using a parabolic exciton dispersion $E_S(Q) = E_S(0) + \frac{\hbar^2 Q^2}{2M_S}$ (M_S is the exciton mass),[1] and introduce the polar coordinates Q and ϕ, such that $Q_x = Q\cos\phi$ and $Q_y = Q\sin\phi$.

The radiative rate in eq. 13 can thus be rewritten as:

$$\gamma_S(Q,\phi) = \gamma_S(0)\cdot\left[\sqrt{1-\frac{c^2Q^2\hbar^2}{E_S^2(Q)}} + \frac{c^2Q^2\hbar^2}{2E_S^2(Q)}\cdot\frac{1-2\cos\phi\,\sin\phi}{\sqrt{1-\frac{c^2Q^2\hbar^2}{E_S^2(Q)}}}\right] \tag{15}$$

The thermally averaged radiative rate for an exciton in state S is defined as:

$$\langle\gamma_S\rangle = \frac{\int_0^{2\pi}d\phi\,\int_0^{Q_0}dQ\,Q\,\gamma(Q,\phi)\,e^{-\Gamma_S(Q)/k_BT}}{\int_0^{2\pi}d\phi\,\int_0^{\infty}dQ\,Q\,e^{-\Gamma_S(Q)/k_BT}} \tag{16}$$

with $\Gamma_S(Q) = E_S(Q) - E_S(0) = \frac{\hbar^2Q^2}{2M_S}$ the kinetic energy of the exciton. The denominator can be integrated to give $\frac{2\pi M_S k_B T}{\hbar^2}$. To compute the numerator, we define the maximum exciton kinetic energy $\Delta_S = \frac{\hbar^2Q_0^2}{2M_S} \approx \frac{E_S(0)^2}{2M_Sc^2}$, change variable from Q to Γ_S, and Taylor expand the exponential up to first order in Γ_S/k_BT as justified by the fact that the maximum value of Γ_S is $\Delta_S \ll k_BT$, given that Δ_S is typically of order 10^{-5} eV. Since the integral over ϕ of the $2\cos\phi\sin\phi$ factor in eq. 15 is zero, the numerator becomes:

$$\frac{2\pi M_S}{\hbar^2}\gamma_S(0)\int_0^{\Delta_S} d\Gamma_S\left(\sqrt{1-\frac{\Gamma_S}{\Delta_S}} + \frac{1}{2}\frac{\frac{\Gamma_S}{\Delta_S}}{\sqrt{1-\frac{\Gamma_S}{\Delta_S}}}\right)\left(1-\frac{\Gamma_S}{k_BT}\right)$$

$$= \frac{2\pi M_S}{\hbar^2}\gamma_S(0)\left(\frac{4}{3}\Delta_S - \frac{4}{5}\frac{(\Delta_S)^2}{k_BT}\right) \tag{17}$$

We thus obtain the thermally averaged exciton radiative lifetime as:

$$\langle\gamma_S\rangle = \gamma_S(0)\left[\frac{4}{3}\left(\frac{\Delta_S}{k_BT}\right) - \frac{4}{5}\left(\frac{\Delta_S}{k_BT}\right)^2\right] \tag{18}$$

Since $\frac{\Delta_S}{k_BT}$ is of order $10^{-1} - 10^{-2}$ at low temperature (4 K, as considered in the main text) and $10^{-3} - 10^{-4}$ at room temperature (300 K), we can neglect the contribution from the term of order $\left(\frac{\Delta_S}{k_BT}\right)^2$.

We conclude that the exciton radiative lifetime can be computed as:

$$\boxed{\langle \gamma_S \rangle = \gamma_S(0) \cdot \frac{4}{3} \left(\frac{\Delta_S}{k_B T} \right) = \gamma_S(0) \cdot \frac{4}{3} \left(\frac{E_S^2(0)}{2 M_S c^2 k_B T} \right)} \tag{19}$$

which is equivalent to the lifetime in eq. 3 in the main text. We remark that no approximations have been made to derive this equation, apart from neglecting terms of order $\left(\frac{\Delta_S}{k_B T}\right)^2$.

When applied to 1D systems, the theory developed so far is equivalent to that employed by Spataru et al.[1] to obtain radiative lifetime in excellent agreement with experiments for carbon nanotubes. Finally, we remark that the MoS_2 bulk lifetime calculation shown here assumes a 2D exciton dispersion, justified by the much larger effective mass along the plane-normal direction than the in-plane directions. Extension of the theory to anisotropic exciton masses in 3D may lead to a more accurate treatment of the bulk case, and will be the subject of future investigation.

References

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(2) Dennery, P.; Krzywicki, A. *Mathematics for Physicists*; Courier Dover Publications, 1996.